

Formation energy in σ -phase Fe-V alloys

J. Cieslak,* J. Tobola, and S. M. Dubiel

AGH University of Science and Technology, Faculty of Physics and
Applied Computer Science, al. Mickiewicza 30, 30-059 Krakow, Poland

(Dated: March 4, 2013)

Formation energy of the σ -phase in the Fe-V alloy system, ΔE , was computed in the full compositional range of its occurrence ($\sim 34 \leq x \leq \sim 60$) using the electronic band structure calculations by means of the KKR method. ΔE -values were found to strongly depend on the Fe concentration, also its variation with different site occupancies was characteristic of a given lattice site. Calculated magnetic, S_{magn} , and configuration, S_{conf} , entropy contributions were used to determine sublattice occupancies for various compositions and temperatures. The results agree well with those obtained from neutron diffraction measurements.

PACS numbers: 71.15.Nc 61.43.-j, 71.20.Be, 71.23.-k, 74.20.Pq, 75.50.Bb,

I. INTRODUCTION

Sigma (σ) phase was found in over 40 binary alloys and many other three- or multi-component alloy systems^{1,2}. The phase cannot be formed at the stage of solidification of the solution of alloying elements. Instead, it can only be obtained by a high temperature annealing process (solid state reaction). From the viewpoint of technological applications of alloys, the σ -phase should be avoided as its presence drastically deteriorates different mechanical properties of materials in which it precipitates. A better knowledge of conditions of its formation may be helpful for fabrications of materials in which the unwanted phase does not precipitate or its precipitation is significantly retarded. On the other hand, due to its complexity (30 atoms per unit cell, five different sublattices, high (12-15) coordination numbers, and lack of a stoichiometry) make the σ -phase a very challenging object for theoretical calculations. They are very helpful for a proper interpretation of measurements, especially those done by means of microscopic methods like Mössbauer spectroscopy or nuclear magnetic resonance, as well as for a better understanding of the results obtained.³⁻⁶

In the Fe-V system the σ -phase can be formed by an isothermal annealing of the *bcc*-master alloys in a wide range of concentration ($\sim 34 - 60$ at.% V) and temperature ($\sim 400 - 1230^\circ\text{C}$)¹. Once formed, it remains stable at lower temperatures, but it can be dissolved into the α -phase at temperatures above $\sim 1230^\circ\text{C}$. Mechanism of its formation as well as that of its dissolution is not known with sufficient precision yet. Knowledge of the energy of its formation compared to the energy of formation of the α -phase (from which it precipitates) may help to better understand processes responsible for its formation and dissolution. Thus, it may be useful in a fabrication of a new generation of materials, like stainless steels, having suitable properties for a construction of new generations of industrially important facilities.

Having a tetragonal unit cell and hosting 30 atoms distributed over five crystallographically non-equivalent sites (usually termed A through E) this phase remains still challenging for theoretical calculations. Luckily, in-

crease of computing capabilities of modern computers makes it possible that more sophisticated models can be applied to more adequately and precisely describe the complex structure and properties of the σ -phase⁷⁻¹⁰.

II. COMPUTATIONAL DETAILS

The present analysis of the structural stability of the σ -phase was based on electronic structure calculations, similar to the methodology applied for σ -FeV and σ -FeCr alloy systems to study hyperfine interactions^{3,4,6,11} as well as the formation energy for the latter⁵. We have employed the Korringa-Kohn-Rostoker (KKR) technique¹²⁻¹⁴ to calculate the electronic structure and the total energy in the framework of the non-relativistic LDA theory and using the muffin-tin approximation for a crystal potential. More computational details on σ -phase can be found in Refs. 3 and 4.

Since in the real structure of σ -FeV all five crystallographic sites are occupied by both types of atoms, a chemical disorder on these sublattices must be taken into account. A more sophisticated approach based on the KKR method with the coherent potential approximation (CPA), allowing to treat the disorder as random, should be capable of accounting for 2^{30} atomic configurations, a target that still remains unreachable. In these circumstances, an alternative, but a feasible approach consists in selection of some ordered elementary unit cells with different configurations of atoms on the five sublattices, which permits to use the KKR method (instead of KKR-CPA one). In practice, the electronic structure calculations were performed for a finite number of the unit cells with a symmetry reduced to a simple tetragonal one (P1 instead of P4₂/mm), in which each position (but not the sublattice) was occupied by one type of atoms (Fe or V). The atoms were distributed over the five different sites with the probabilities determined from neutron diffraction measurements¹⁵ which were next altered in the way described below. Differences between total energies (per atom), ΔE (usually called the formation energy), determined for each of these atomic configurations, E_σ , and

corresponding values obtained for pure constituents, i.e. *bcc*-Fe and *bcc*-V, E_α , could be calculated¹⁶ according to Eq. (1):

$$\Delta E = E_\sigma - (1-x)E_\alpha^{Fe} - xE_\alpha^V \quad (1)$$

where x stands for the concentration of V. They can be further presented in form of a diagram as a function of concentration of the alloying elements. This approach was already successfully applied to the analysis of the formation energy of the σ -phase in the Fe-Cr alloy system⁵.

As mentioned above, the σ -phase is characterized by a chemical disorder on all five sublattices, and the concentrations of Fe/V atoms on each of them were determined experimentally¹⁵. Since both Fe and V atoms are present on all five sublattices, it is useful for further considerations to introduce shortened notations for samples with different sublattice occupancies. Multiplicity (denoted by N_i) of the five Wyckoff positions, namely 2a, 4f, 8i, 8i' and 8j correspond to A, B, C, D and E site, respectively. Since the total number of atoms on each of the five sublattices was already known, thus it was enough to indicate the number of the Fe atoms on each sublattice explicitly, while the V atoms constitute the balance. According to this convention, an illustrative example of σ -20172 describes a system comprising 2, 1, 7, and 2 atoms of Fe on the sites A, C, D and E, respectively, and also 4, 7, 1 and 6 atoms of V atoms on the sites B, C, D and E.

In the present work we analyzed more carefully ordered unit cells corresponding to the following atomic configurations: σ -20172, σ -20383 and σ -21485. The total number of Fe atoms in them is 12, 16 and 20, respectively. The three configurations have been chosen intentionally to best approximate experimentally investigated samples viz. $\text{Fe}_{41}\text{V}_{59}$, $\text{Fe}_{52}\text{V}_{48}$ and $\text{Fe}_{66}\text{V}_{34}$, respectively⁶. These three cases correspond to the border and middle compositions of the σ -phase existence on the phase diagram of the Fe-V alloy system¹⁷. Actually, we treated these configurations as the reference for a further analysis of ΔE .

In the next step we have calculated the ΔE -values, for the unit cells changed (with respect to the three reference ones) by a replacement of one or two atoms exclusively on the same site. Ten ordered approximants of each configuration of sublattice occupancies with different atomic arrangements were analyzed, and average ΔE -values, obtained in this approach for neighborhoods of the three reference configurations, are presented as a function of Fe atoms number per unit cell, n_{Fe} (Fig. 1). Simultaneously, the ΔE -changes caused by the replacements of atoms on each sublattice are indicated with various colors.

III. RESULTS AND DISCUSSION

The changes of ΔE in the vicinity of the three reference configurations are fairly linear functions of n_{Fe} for

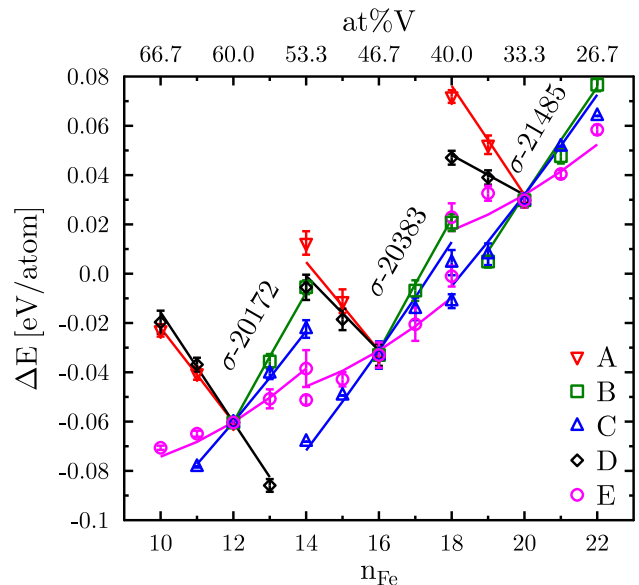


FIG. 1: (Online color) Calculated formation energy differences for the Fe-V σ -phase, ΔE , for the chosen three basic atomic configurations and its neighborhood, versus the number of Fe atoms per unit cell, n_{Fe} (V concentration is also indicated). Solid lines stand for the best fit to the data - see Appendix. ΔE -values determined for occupation changes (with respect to the reference configurations) on the five lattice sites are indicated by different colors.

the sites A, B, C, and D, and rather non-linear for the site E. The slopes of the lines for the sites A, B and C are characteristic of the site and equal -0.021(1), 0.025(1) and 0.019(1) - in eV/atom - respectively. Interestingly, these slopes are more or less the same for all reference configurations (see, Fig. 1), while for the site D the value of the slope depends on the alloy basic configuration around which it is calculated (changes from -0.022 for σ -20172 to -0.009 eV/atom for σ -21485). ΔE corresponding to the changes on the site E departs from linearity and can be approximated using a second-order polynomial of the Fe-concentration on this site.

The model used for the formation energy calculation allowed to determine the values of ΔE only for such cases, in which individual sites (but not sublattices) are occupied by just one type of atoms. This really corresponds to a one selected unit cell, whereas in the neighboring cells atoms may be arranged in a somewhat different way on the sublattices. For that reason, for a more realistic description of crystalline samples it is more convenient to operate with the average formation energy that corresponds to the average occupancy of the sublattices by the alloying elements. As shown in Fig. 1, ΔE have been determined for almost 50 different configurations of Fe and V atoms, including - to some extent - the chemical disorder on the sublattices. The relatively simple character of the ΔE -changes described above (mostly linear behav-

ior), provides a possibility of determining a dependence of ΔE on the Fe-concentrations, x_i , $i = A$ through E , on each sublattice. It can be achieved by approximation of ΔE using a function depending on the variables x_i , on five individual sites, $\Delta E = \Delta E(x_A, x_B, x_C, x_D, x_E)$. Taking into account the established character of the ΔE -changes, there were assumed to be linear (A through D sites), and quadratic (E site) dependences on x_i (see Appendix). Fitting such-defined functions to the calculated ΔE -values (using the least-square method) yielded numerical values of polynomial coefficients. Consequently, it allowed to determine ΔE for any atomic configuration for all five sites in the σ -FeV structure.

A. Entropy contributions

Bearing in mind that the aforementioned total energy E and the electronic structure analysis correspond, in principle, to ground state properties, one can attempt to discuss crystal stability at finite temperature T , applying commonly used scheme based on a computation of the free energy, $F = E - TS$, where S stays for an entropy. Considering the process of the σ -phase formation, one can discuss $\Delta F = \Delta E - TS$, being the difference between the free energy of σ -FeV alloy and free energies of its constituents (namely, weighted contributions of a pure bcc Fe and V which are already known).

The total entropy that actually should be taken into account in the present case has several contributions, namely: magnetic entropy, S_{mag} , configuration entropy, S_{conf} , electronic entropy, S_{el} , and phonon entropy, S_{ph} . The first two terms could be computed, and the results of these computations are shown in Fig. 2, for the magnetic entropy, and in Fig. 3, for the configuration one.

Using the magnetic moments maximum saturation entropy for each atom on the sublattice, $S_{mag}^{max} = k_B \ln(2J + 1)$, can be determined¹⁸. In this work S_{mag} -values were calculated according to the following Eq. (2):

$$S_{mag} = k_B \sum (P_i \ln(\mu_i^{Fe} + 1) + (1 - P_i) \ln(\mu_i^V + 1)) \quad (2)$$

where k_B is the Boltzmann constant, P_i stands for the occupancy of Fe on each sublattice, μ_i is the average magnetic moment of Fe/V atoms belonging to this sublattice and summation (i -index) runs over all five sublattices i.e. from A to E. μ_i -values for each sublattice and different x_i configurations were obtained from the electronic structure KKR calculations. Fig. 2 gives a clear evidence that for each sample S_{mag} increases with n_{Fe} for each lattice site. The increase of the magnetic entropy remains in line with our previous calculations reporting that the magnetic moments (also the hyperfine fields) at particular sites increase with n_{Fe} ⁶. Similarly to the ΔE expression, S_{mag} can be represented as a function of x_i , $S_{mag} = S_{mag}(x_A, x_B, x_C, x_D, x_E)$. Although changes in S_{mag} due to changes in the individual site occupancies are monotonic, however, they deviate slightly from

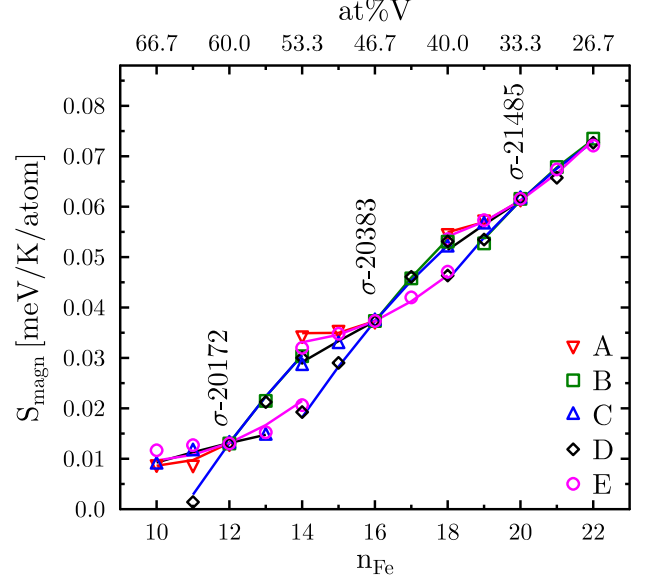


FIG. 2: (Online color) The magnetic entropy, S_{mag} , calculated versus the number of Fe atoms per unit cell, n_{Fe} , for different atomic configurations (samples) of the σ -FeV. The concentration of vanadium is indicated, too. Solid lines stand for the best fit to the data - see Appendix. S_{mag} -values determined for occupation changes on the individual lattice site are indicated by different colors.

linearity. To approximate the S_{mag} dependence on x_i , we assumed a mathematical form of the function analogous to that used for ΔE (see Appendix). The numerical values of the polynomial coefficients were determined by fitting the function to the calculated S_{mag} -values.

The configuration entropy, shown in Fig. 3, was calculated according to Eq. (3):

$$S_{conf} = -k_B \sum (P_i \ln(P_i) + (1 - P_i) \ln(1 - P_i)) \quad (3)$$

It shows a strong dependence on the site for each of three basic configurations. The dependence is very similar for the sites A, B and C, while S_{conf} for the other two sites i.e. D and E depends on n_{Fe} in a way characteristic of the reference configuration. Eq. 3 shows that the configuration entropy, S_{conf} , can be easily calculated for any concentration of atoms on all sites, $S_{conf} = S_{conf}(x_A, x_B, x_C, x_D, x_E)$.

B. Free energy contribution

The knowledge of ΔE , S_{mag} and S_{conf} for any concentration of Fe in the sublattices allows to specify a formula describing a change of the free energy, $\Delta F = \Delta E - T(S_{mag} + S_{conf})$ for any concentration of the alloying elements, and any temperature, $\Delta F = \Delta F(x_A, x_B, x_C, x_D, x_E; T)$. Determination of the lowest

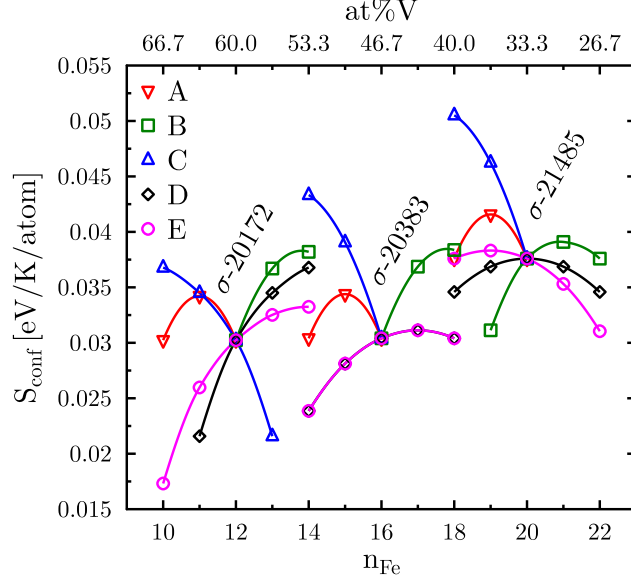


FIG. 3: (Online color) The configuration entropy, S_{conf} , calculated versus the number of Fe atoms per unit cell, n_{Fe} , for different atomic configurations of the σ -FeV. The concentration of vanadium is indicated, too. S_{conf} -values determined for the occupation changes at each lattice site are plotted using different colors.

value of this function for the given temperature and concentration, allowed to determine sublattice occupancies, P_i at the temperature T and Fe-concentration $x_{Fe} = \frac{1}{30} \sum_i N_i P_i$ (where N_i denotes the occupation number for the sublattice i). The P_i -values calculated for some chosen concentrations are shown in Fig. 4 for the temperature ranging between 0 and 1800 K. At the first glance, one notices a significant site preference for the occupancies in the investigated phase. In particular, one can clearly see that the Fe occupancy of the sites A and D is actually complete and independent of the concentration and temperature. The occupancy variation with x and T is significantly larger for the other sites. It was found that increasing of x_{Fe} in the alloy results in an increase of Fe content mainly on the sites C and E. For the latter, one can observe the highest sensitivity to temperature (P_E decreases with temperature) in comparison to much slower variations revealed for B and C site occupancies (that increase with temperature).

It should be noted that the entropy contribution that predominantly effects the sublattice occupancies is the configuration entropy term. Neglecting S_{mag} in the calculation of P_i , depending on x and T as shown in Fig. 4, leads to very small changes. It becomes clear when accounting for a similarity of all individual curves presented in Fig. 2. There, S_{mag} curves vary mainly with the total concentration of Fe/V atoms, and are very similar for all sublattices. This means that this form of the entropy does not substantially affect the site preferences.

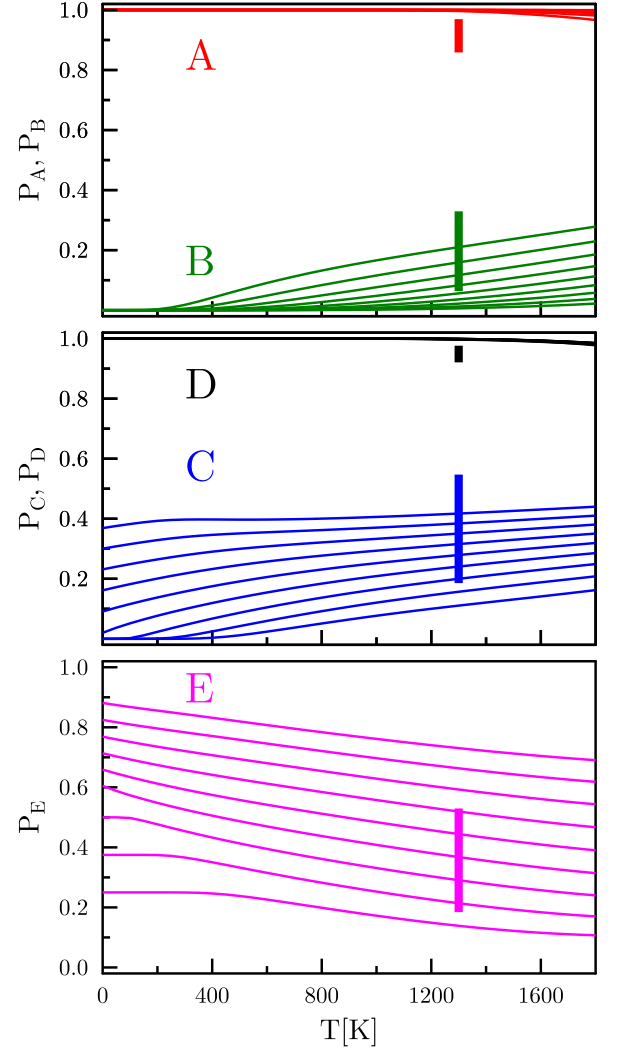


FIG. 4: (Online color) The probability of finding Fe-atoms on the five lattice sites, P_i , versus temperature, T . The solid lines indicate the calculated values for different compositions of the σ -Fe $_{100-x}$ V $_x$ with x ranging from 33 to 60 (the curves from top to bottom correspond to alloys with increasing x). The vertical bars indicate experimentally found values of P_i in the same concentration range.

The solid lines (Fig. 4) indicate the P_i -values calculated for different compositions of the σ -Fe $_{100-x}$ V $_x$ with x ranging from 33 to 60 (full range of σ -FeV occurrence). Vertical bars - marked in the plots - indicate values of P_i as determined at RT, but for the samples transformed to the σ -phase at 1300 K (that is why the bars are marked at this temperature in the plot). As the figure shows, the site occupancies calculated by the minimization of the free energy fairly agree with the values obtained from the neutron diffraction experiments. The agreement between theory and experiment is less satisfying for the site

E, since the calculated P_i -curves span over a wider range than the the width of the corresponding bar.

The discrepancy observed between the calculated and experimental P_i -values is likely due to several factors. One of them is the simplified model used for the entropy calculations viz. without taking into account the phonon and the electron entropy terms. However, a possible influence of these terms on final results seems to be rather small as previously found from the formation energy analysis of the σ -phase in the Fe-Cr alloy system⁵. Unfortunately, we are not aware of any literature data reporting vibrational properties of the σ -FeV that would allow to estimate the S_{ph} contribution. On the other hand, bearing in mind a similarity of atomic and lattice parameters for Fe-V and Fe-Cr σ -phases, it seems reasonable to assume that the S_{ph} contribution to the total entropy is also small in the present case. The effect of the S_{el} term was not taken into account mostly due to the fact that our discussion was focused on temperatures ~ 1300 K that are far above the Debye temperature of the investigated samples ($\sim 400 - 600$ K¹⁹).

Another factor that could be responsible for the discrepancy between the calculated and the experimental P_i - values is the assumed form (polynomials) of the functions for the ΔE and S_{mag} (hence, in consequence that of ΔF). Better fits were obtained by increasing the degree of the used polynomials, but in that case the discrepancy was not improved.

IV. SUMMARY

The formation energy, ΔE , magnetic, S_{mag} , and configuration, S_{conf} , entropy contributions were calculated and analyzed in the full range of the FeV- σ -phase existence using the electronic band structure calculations by means of the KKR method. It was found that ΔE -values strongly depend on the Fe concentration, and their variation observed for different site occupancies is characteristic of a given lattice site. The changes also strongly depend on the number of Fe atoms on the sites. Similar, increasing dependence on the sample's composition exhibits the S_{mag} term, but for a given composition it weakly depends on the lattice site. On the other hand, the composition dependence of the S_{conf} term was found to be weak, although for a given composition, S_{conf} , shows well-defined dependence on the lattice site, and for each site, a rather strong dependence on the number of Fe atoms occupying the site. The sublattice occupancies were determined for various compositions and temperatures by minimizing the free energy. The occupancies of A and D sites were found to be almost independent of T and x , while the occupancies of the sites B, C and D showed a higher sensitivity to T and x . The KKR calculations combined with the analysis of the entropy contributions clearly showed that Fe atoms preferably occupy A and D sites in the FeV- σ phase. This agrees well with the neutron diffraction measurements, and it

confirms the general observation for σ in binary alloy systems that the smaller atoms (in this case Fe) tend to mostly reside on the sites having the shortest distance to the nearest-neighbors (A and D), while the bigger atoms (here V) prefer to occupy the sites having more free space to accommodate them (B, C, E).

Acknowledgments

This work, supported by the European Communities under the contract of Association between EURATOM and IPPLM, was carried out within the framework of the European Fusion Development Agreement. It was also supported by the Ministry of Science and Higher Education, Warsaw (grant No. N N202 228837). We also acknowledge financial support from the Accelerated Metallurgy Project, which is co-funded by the European Commission in the 7th Framework Programme (contract NMP4-LA-2011-263206), by the European Space Agency and by the individual partner organizations.

Appendix A: Nomenclature

There are several possibilities for description of sublattice occupancy in the FeV σ -phase.

One can directly indicate n_i ($i = A$ through E), the number of Fe atoms occupying each site. Using that, $\sum n_i = n_{Fe}$ gives the total number of Fe atoms in the unit cell and $\frac{1}{30} \sum n_i$ gives the total concentration of iron.

Sublattice occupancy by Fe atoms can be easily calculated here as $x_i = n_i/n_{Fe}$ (in other words x_i stands for the probability that randomly chosen Fe-atom belongs to the sublattice i , $\sum x_i = 1$).

On the other hand, $P_i = \frac{n_i}{N_i}$ (N_i being the multiplicity of the i -th sublattice) denotes Fe-concentration on i -th sublattice (the probability, that randomly chosen atom on i -th sublattice is iron).

Appendix B: Polynomial coefficients

From the fitting procedure ΔE (in [eV/atom]), and S_{mag} (in [eV/K/atom $\times 10^{-8}$]) were determined, as follows:

$$\begin{aligned} \Delta E = & 0.17446 - 0.03178n_1 + 0.01269n_2 \\ & - 0.03404n_3 + 0.00768n_4 - 0.00689n_5 \\ & + 0.00258n_5^2 \\ & + 0.00226n_3(n_1 + n_2 + n_4 + n_5) \\ & - 0.00160n_5(n_1 + n_2 + n_4 + n_5) \end{aligned} \quad (B1)$$

$$S_{mag} = -1525.45 - 199.617n_1 + 247.216n_2$$

$$\begin{aligned}
& +195.366n_3 + 624.922n_4 + 137.535n_5 \\
& +62.3663n_5^2 - 46.5917n_4^2 - 11.4958n_3^2 \\
& \quad -56.8196n_2^2 + 117.045n_1^2 \\
& +287.426n_1n_2 + 35.9117n_1n_3 \\
& -72.3616n_1n_4 + 0.05473n_1n_5 \\
& +41.4487n_2n_3 - 3.62722n_2n_4 \\
& -63.1291n_2n_5 + 95.9298n_3n_4 \\
& -7.77130n_3n_5 - 38.1694n_4n_5 \quad (B2)
\end{aligned}$$

-
- * Corresponding author: cieslak@fis.agh.edu.pl
- ¹ E. D. Hall and S. H. Algie, *Metall. Rev.* **11**, 61 (1966).
 - ² J.-M. Joubert *Progr. Mater. Sci.* **53**, 528 (2008).
 - ³ J. Cieslak, J. Tobola, S. M. Dubiel, S. Kaprzyk, W. Steiner and M. Reissner, *J. Phys.: Condens. Matter* **20**, 235234 (2008).
 - ⁴ J. Cieslak, J. Tobola, and S. M. Dubiel, *Phys. Rev. B* **81**, 174203 (2010).
 - ⁵ J. Cieslak, J. Tobola, and S. M. Dubiel, *Intermetallics* **24**, 84 (2012).
 - ⁶ J. Cieslak, J. Tobola, and S. M. Dubiel, *Intermetallics* **22**, 7 (2012).
 - ⁷ E. A. Kablman, A. A. Mirzoev and A. L. Udovskii, *Phys. Met. Metallography* **108**, 435 (2009).
 - ⁸ J. Pavlů, J. Vřešťál and M. Šob, *Intermetallics* **18**, 212 (2010).
 - ⁹ E. Kablman, P. Blaha, K. Schwarz, A. V. Ruban and B. Johansson, *Phys. Rev. B* **83**, 092201 (2011).
 - ¹⁰ E. Kablman, P. Blaha, K. Schwarz, O. E. Peil, A. V. Ruban and B. Johansson, *Phys. Rev. B* **84**, 184206 (2011).
 - ¹¹ J. Cieslak, J. Tobola, S. M. Dubiel and W. Sikora, *Phys. Rev. B* **82**, 224407 (2010).
 - ¹² T. Stopa, S. Kaprzyk, and J. Tobola, *J. Phys.: Condens. Matter* **16**, 4921 (2004).
 - ¹³ A. Bansil, S. Kaprzyk, P. E. Mijnarends, and J. Tobola, *Phys. Rev. B* **60**, 13396 (1999).
 - ¹⁴ S. Kaprzyk and A. Bansil, *Phys. Rev. B* **42**, 7358 (1990).
 - ¹⁵ J. Cieslak, M. Reissner, S. M. Dubiel, J. Wernisch and W. Steiner, *J. Alloys Comp.* **460**, 20 (2008).
 - ¹⁶ P. E. A. Turchi 12th National Conference on "Phase Diagrams, Materials Design and its Applications", UCRL-PROC-206980 (2004).
 - ¹⁷ O. Kubaschewski, *Iron Binary Phase Diagrams* by Springer, (Berlin 1982).
 - ¹⁸ Y. Chuang, R. Schmid and Y. A. Chang, *Metall. Trans. A* **16a**, 153 (1985).
 - ¹⁹ J. Cieslak, M. Reissner, S. M. Dubiel, B. F. O. Costa and W. Steiner, *Intermetallics* **18**, 1695 (2010).